



Durability and rejuvenation of electrochromic tungsten oxide thin films in LiClO_4 -propylene carbonate viscous electrolyte: Effect of Ti doping of the film and polyethylene oxide addition to the electrolyte

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ABSTRACT

Tungsten oxide and titanium doped tungsten oxide thin films, deposited by sputtering, were immersed in a viscous electrolyte comprised of LiClO_4 in propylene carbonate and 2.0 wt% of polyethylene oxide (PEO). Electrochromic properties of the films were investigated by electrochemical techniques and in situ transmittance measurements. Cyclic voltammetry data were taken in the voltage ranges 2.0–4.0 and 1.5–4.0 V vs Li/Li^+ for up to 500 cycles. A potentiostatic rejuvenation treatment was then performed on the degraded electrochromic films, at 6.0 V for 20 h, which was subsequently followed by another cyclic voltammetry measurement. Titanium incorporation into tungsten oxide resulted in a small cyclic stability improvement in the 2.0–4.0-V range, whereas less pronounced effects were observed for cycling in the 1.5–4.0-V range. Combining the results of the present study with our previous work, we are able to assess the relative merits of titanium incorporation and PEO addition to the electrolyte for the durability of electrochromic tungsten oxide thin films. Titanium addition was found advantageous for electrochemical durability in the 2.0–4.0-V range, but no clear benefits of PEO in the electrolyte were seen. On the other hand, in the wider 1.5–4.0-V range, tungsten oxide exhibited better durability than titanium-containing films, and this was especially so after rejuvenation in the PEO-containing electrolyte.

1. Introduction

Buildings currently account for around 36% of global energy use [1]. Therefore, improving energy efficiency in buildings is an essential element in current efforts to mitigate climate change [2]. In particular, the impact of windows and glass facades (known as glazing) on energy efficiency is significant in buildings. Dynamic glazing, with switchable optical properties, controls the solar energy entering the building and thus provides substantial energy savings [3–6]. Electrochromic (EC) glazing is the most commonly used dynamic glass technology [5].

The most common type of EC glazing is made up of five superimposed layers on a substrate such as glass or flexible polymer sheets, or sandwiched between two such substrates [7–10]. The ion conductive layer is made of a transparent electrolyte—either a thin inorganic film or a polymeric layer—and is placed at the center of the EC glazing

configuration. A cathodically coloring EC layer such as W oxide is positioned on one side of the center layer and an anodic layer such as Ni oxide or V oxide is placed on the other side [11–17]. These three layers are surrounded by transparent and electrically conductive layers (TCO)—based on In oxide or Sn oxide—which are used as electrical contacts. Applying a voltage between the TCO layers, electrons from the TCO and ions in the electrolyte are inserted into the cathodic EC layer and coloration occurs. Simultaneously, coloration takes place by ion and electron extraction from the anodic EC layer. The colored state remains until the voltage is reversed, which causes electrons and ions to move back, so that the EC glazing turns transparent again.

Longevity is essential for the successful commercialization of EC glazing, and much prior research and development has been devoted to studies of durability under extended cycling between transparent and dark states for individual EC layers as well as full EC devices; advances

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were surveyed recently [18,19]. By incorporation of admixtures or dopants into W oxide and Ni oxide thin films, notably Ti into W oxide [20–25] and Ir or Ta into Ni oxide [26,27], cycling durability and lifetime were improved. In particular, it has been demonstrated several times that additions of titanium provide increased structural and electrochemical stability to WO_3 [20,22,23]. In our previous work, we have confirmed that Ti incorporated WO_3 films showed superior electrochromic properties and durability, as compared to pristine WO_3 thin films [24,25]. However, the EC properties of Ti doped WO_3 show a widespread performance in terms of charge capacity and coloration efficiency. It should be noted that the charge capacity depends on thickness and porosity and is often not normalized to take into account variations in microstructure. The coloration efficiency shows a large spread [23,24,28] but it is difficult to make an intercomparison since it has been reported at different wavelengths in different papers. The reported EC properties range from poor charge capacity together with a very high coloration efficiency [29] to films deposited at carefully optimized sputter conditions [30] and post-annealing treatments [31], displaying a high optical contrast between colored and bleached states as well as a good coloration efficiency.

Furthermore, films with degraded EC performance—caused by Li trapping [32–34]—can be rejuvenated by potentiostatic or galvanostatic post-treatment [35–40], and interfacial layers (so called “solid-electrolyte interphases” made by potential pretreatment [41,42] or self-assembly [43]) can improve durability. However, durability is a complex and multifaceted property and depends critically on the EC films, the electrolyte, and the details of their interactions. In a previous article [44], we investigated the degradation of W oxide films in LiClO_4 -propylene carbonate (PC) electrolyte. It was found that the viscosity increased monotonically from ~ 0.1 Pa s in the absence of polyethylene oxide (PEO), to ~ 5 Pa s for 1.0 wt% PEO and ~ 200 Pa s for 3.0 wt% PEO. The results showed that adding a few wt% of PEO to the electrolyte was beneficial for durability. In particular, the largest optical modulation after electrochemical rejuvenation was achieved for W oxide films in an electrolyte with PEO additions between 1.5 and 2.5 wt%.

The present investigation aims to assess the relative merits of the combination of Ti addition to the film and PEO addition to the electrolyte for electrochromic durability and potentiostatic rejuvenation of W-oxide-based thin films. We build on our previous studies of the durability and potentiostatic rejuvenation of Ti incorporated W oxide thin films [24] and the effect of PEO in LiClO_4 -PC electrolytes on the durability and rejuvenation of EC W oxide thin films [44]. Below, we present results on the effect of Ti incorporation into W oxide films on EC properties after potentiostatic rejuvenation in 1 M LiClO_4 -PC having 2.0 wt% of PEO and compare them to our previous studies [24,44]. These combined results give a clear view of how the effects of Ti addition and electrolyte modification interplay and influence the electrochemical durability of W-oxide-based EC films.

2. Experimental

Reactive DC magnetron sputtering was employed for deposition of W oxide thin films with and without incorporation of Ti, by using a Balzers UTT 400 unit. The EC films were deposited onto $\text{In}_2\text{O}_3\text{:Sn}$ (ITO, 60 Ω /square) coated glass using 5-cm-diameter targets of tungsten (having 99.95% purity), tungsten (95 wt%)-titanium (5 wt%), and tungsten (90 wt%)-titanium (10 wt%), and using a ~ 13 cm distance between the target and substrate. First, the deposition chamber was pumped down to a pressure of $\sim 10^{-7}$ Torr, and eventual contaminations on the surface of the sputtering targets were removed by pre-sputtering in argon (99.997%) for several minutes. Argon and oxygen (99.97%) were then introduced into the deposition system via mass-flow-controlled inlets. The total gas pressure during sputtering was 30 mTorr and the O_2/Ar ratio was kept at 0.133. Sputtering was performed onto unheated substrates applying a power of 200 W. Film thickness uniformity was

assured by substrate rotation during deposition. The thickness of the thin films, as measured by a Bruker Dektak XT surface profilometer, was 300 ± 20 nm. Transmittance spectra of as-deposited films, in the wavelength range between 300 nm and 2500 nm, were acquired by a PerkinElmer Lambda 900 spectrophotometer.

X-ray diffraction (XRD) measurements were performed by a Siemens D5000 diffractometer using $\text{CuK}\alpha$ radiation with wavelength $1.54 \text{ \AA}$. A scanning electron microscope (SEM) (Zeiss LEO-1530, using an acceleration voltage of 10 kV) was used to obtain images of the films' surfaces.

The electrolyte was a mixture of LiClO_4 (98%, Alfa Aesar), PC (99%, Sigma-Aldrich), and PEO with average molecular weight of 4,000,000 (Sigma-Aldrich). A 1 M solution was prepared by dissolving LiClO_4 in PC by stirring at room temperature. PEO was then added to a concentration of 2.0 wt% and the resulting solution was mixed for ~ 20 h at 75°C . The mixture was continuously stirred until reaching room temperature. The viscosity of the electrolyte was ~ 75 Pa s [44].

Cyclic voltammetry (CV) measurements were performed using a BioLogic SP-200 potentiostat. Reference and counter electrodes were Li foils, and films of W oxide and Ti-W oxide on ITO-coated glass were used as working electrodes. In this study, all potentials are given vs Li/Li^+ . First, the films were scanned for 500 and 100 cycles at a rate of 20 mV s^{-1} in the potential ranges 2.0–4.0 and 1.5–4.0 V, respectively. To rejuvenate the degraded EC films, potentiostatic post-treatments were performed by applying a potential of 6.0 V for 20 h, an applied potential higher than the one used for bleaching the films. To regain electrochemically stable conditions, the samples were maintained at open circuit potential for 2 h. This rejuvenation treatment was followed by CV measurements for 300 cycles in the 2.0–4.0-V range and 500 cycles in the 1.5–4.0-V range with a scan rate of 20 mV s^{-1} . Simultaneous in-situ optical transmittance measurements were performed at a wavelength of 528 nm and were normalized to the transmittance with only electrolyte in the cell. A light emitting diode (LED) and a photodiode sensor were used to perform the optical measurements. The LED emitted at a wavelength of 528 nm, which is close to the center of the visible range. The results thus give a reasonable approximation to the average visible transmittance. All spectroelectrochemical measurements were performed in a glove box having an argon atmosphere with less than 1 ppm water content.

3. Results

Structural and morphological information is given in Fig. 1. Panel (a) shows XRD results for W oxide and Ti-W oxide thin films deposited on ITO. Nothing but ITO-dependent features were observed and we infer that the films were amorphous. Elemental compositions of these films were obtained from time-of-flight elastic recoil detection analysis (ToF-ERDA) in earlier work of ours and were reported to be WO_3 , $\text{W}_{0.87}\text{Ti}_{0.13}\text{O}_3$, and $\text{W}_{0.80}\text{Ti}_{0.20}\text{O}_3$ [24]. For clarity, $\text{W}_{0.87}\text{Ti}_{0.13}\text{O}_3$ were deposited by sputtering from the 5 wt% Ti target and $\text{W}_{0.8}\text{Ti}_{0.2}\text{O}_3$ films from the 10 wt% Ti target. Fig. 1(b)–1(d) show SEM images for such films. The surfaces consistently displayed nanoparticle aggregates with linear sizes of ~ 50 – 60 nm. There were no significant effects of Ti incorporation on the surface morphology.

Fig. 2 shows CV measurements performed between 2.0 and 4.0 V in 1 M LiClO_4 -PC electrolyte with 2.0 wt% PEO (panels 2a1–2c1) together with corresponding optical transmittance modulation (panels 2a2–2c2) for films of WO_3 , $\text{W}_{0.87}\text{Ti}_{0.13}\text{O}_3$, and $\text{W}_{0.80}\text{Ti}_{0.20}\text{O}_3$. The measurement was initiated at open-circuit potential and CV data were obtained for cycle numbers between 2 and 500 (solid curves in Fig. 2a1–2c1). CV data after potentiostatic rejuvenation were recorded for 300 additional cycles and selected recordings are shown as dashed curves in Fig. 2a1–2c1. The changes in the shapes and the encircled areas of the CV data indicate that the charge capacity Q evolved during voltammetric cycling. These effects were most apparent during initial cycling, while the results after 400 cycles were rather similar to those after 500

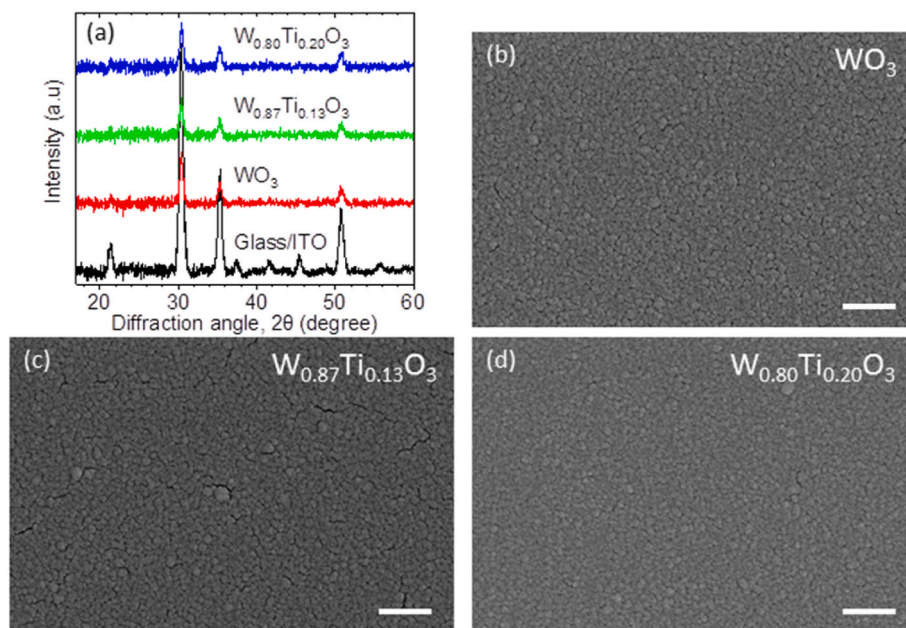


Fig. 1. Structural and morphological data of W oxide and Ti–W oxide with the shown compositions. (a) XRD patterns and (b)–(d) SEM images of ~ 300 -nm-thick films deposited on ITO-coated glass. The scale bars are 500 nm.

cycles.

It is also apparent that the shapes of the CV's display significant differences before and after rejuvenation. The positive current peak and the current onset at the high potential end are shifted to higher potentials, while no clear conclusion can be drawn from the featureless curves at negative currents. The behavior at positive currents is suggestive of an iR-drop due to the presence of an additional resistive layer on the EC film after rejuvenation. This would be consistent with the appearance of a solid-electrolyte interphase during the rejuvenation treatment at a potential of 6 V. However, the appearance of weak subsidiary peaks in the CV's after rejuvenation suggests a more complex mechanism.

The transmittance of the as-prepared films was of the order of the transmittance of the ITO-coated glass substrate, as seen from the spectra shown in Fig. 3. The transmittance at 528 nm ranged from values as low as ~ 30 , ~ 35 , and $\sim 40\%$ in the dark state for films of WO_3 , $\text{W}_{0.87}\text{Ti}_{0.13}\text{O}_3$, and $\text{W}_{0.80}\text{Ti}_{0.20}\text{O}_3$, respectively, to values above 90% in the bleached state (Fig. 2a2–2c2). During CV cycling, the transmittance in the dark state monotonically increased but it remained constant in the bleached state, i.e., the optical modulation range ΔT decreased. After 500 cycles, the transmittance in the colored state was ~ 55 , ~ 51 , and $\sim 58\%$ for films of WO_3 , $\text{W}_{0.87}\text{Ti}_{0.13}\text{O}_3$, and $\text{W}_{0.80}\text{Ti}_{0.20}\text{O}_3$, respectively. Thus, the addition of Ti was found to play a minor role and, at best, yielded a modest increase in durability. After potentiostatic rejuvenation, the dark-state transmittance was ~ 40 , ~ 41 , and $\sim 44\%$ for films of WO_3 , $\text{W}_{0.87}\text{Ti}_{0.13}\text{O}_3$, and $\text{W}_{0.80}\text{Ti}_{0.20}\text{O}_3$, respectively, while the bleached-state transmittance consistently was ~ 93 – 95% . Interestingly, the dark-state transmittance remained almost constant at 40–45% after 300 CV cycles and hence one concludes that Ti incorporation into W oxide thin films can provide stabilized transmittance in the dark state with a desired magnitude after the rejuvenation treatment.

Charge capacity vs cycle number is shown in Fig. 4 for potential scans in the 2.0–4.0-V range. Both inserted and extracted charges are shown; these data are consistent with the information in Fig. 2a1–2c1. Data in panels 4a–4c refer to WO_3 , $\text{W}_{0.87}\text{Ti}_{0.13}\text{O}_3$, and $\text{W}_{0.80}\text{Ti}_{0.20}\text{O}_3$ thin films, respectively. $|Q|$ decreased monotonically upon cycling of the films; the rate of this decline was largest for the film of WO_3 . Rejuvenation consistently brought the charge capacity back to a value that was only slightly smaller than that of the initial reading for the as-deposited film. The charge capacity for the rejuvenated film of $\text{W}_{0.80}\text{Ti}_{0.20}\text{O}_3$ film was

somewhat larger than that of the as-deposited film after ~ 60 cycles. We have also calculated the $\text{Li}/(\text{W} + \text{Ti})$ ratio x in the dark state, assuming a density of the film of 6 g cm^{-2} [22]. The value of x in the first cycles decreases upon Ti addition, from 0.22 for pure WO_3 to 0.195 and 0.17 for films of $\text{W}_{0.87}\text{Ti}_{0.13}\text{O}_3$, and $\text{W}_{0.80}\text{Ti}_{0.20}\text{O}_3$, respectively. This decrease in normalized charge capacity is evidently the reason for the higher dark state transmittances in the initial cycles for the Ti-containing films (Fig. 2 a2–c2). The x -values are slightly lower in the first cycles after rejuvenation, namely in the range of 0.15–0.17.

Fig. 5 is analogous to Fig. 2 but reports data for films subjected to harsh voltammetric cycling between 1.5 and 4.0 V. Panels 5a1–5c1, referring to voltammetry, shows that the CV data are in overall principle agreement with corresponding data taken in the 2.0–4.0-V range (cf. Fig. 2a1–2c1). However, the charge capacity is much larger for cycling between 1.5 and 4.0 V and, most significantly, the decrease of the encircled areas in the voltammograms is much faster for CV cycling in the larger potential range.

Corresponding optical data (Fig. 5a2–5c2) show in detail how the transmittance increased in the colored state and decreased in the bleached state upon voltammetric cycling. As a result, ΔT shrank very sharply and was about 10% of the initial modulation after a few tens of CV cycles. After that, the decline progressed more slowly. Specifically, the initial optical modulation ranges were ~ 78 , ~ 74 , and 68% for films of WO_3 , $\text{W}_{0.87}\text{Ti}_{0.13}\text{O}_3$, and $\text{W}_{0.80}\text{Ti}_{0.20}\text{O}_3$, respectively, whereas the corresponding data were as small as ~ 7 , ~ 8 , and 13% after 100 cycles. Evidently, the addition of Ti could lead to slower degradation of the optical properties of the Ti–W oxide films, but the effect was rather marginal. Potentiostatic rejuvenation increased the bleached-state transmittance for the three films; in the case of WO_3 , it reached 94%. Subsequent cyclic voltammetry demonstrated that the stability of the optical modulation was largely improved after rejuvenation for pure WO_3 , and ΔT was as large as 37% after 500 CV cycles, whereas the stabilizing effect of the rejuvenation treatment was much smaller for $\text{W}_{0.87}\text{Ti}_{0.13}\text{O}_3$, and $\text{W}_{0.80}\text{Ti}_{0.20}\text{O}_3$ exhibited an intermediate result. The results for WO_3 can be compared with ref. 44. There is a small difference in the transmittance values, mainly in the data for the 2.0–4.0-V range, which we do not regard as serious. However, the films in ref. 44 appears to be more stable, especially when cycled in the 1.5–4.0-V range after rejuvenation. This may be due to differences in ageing protocol between

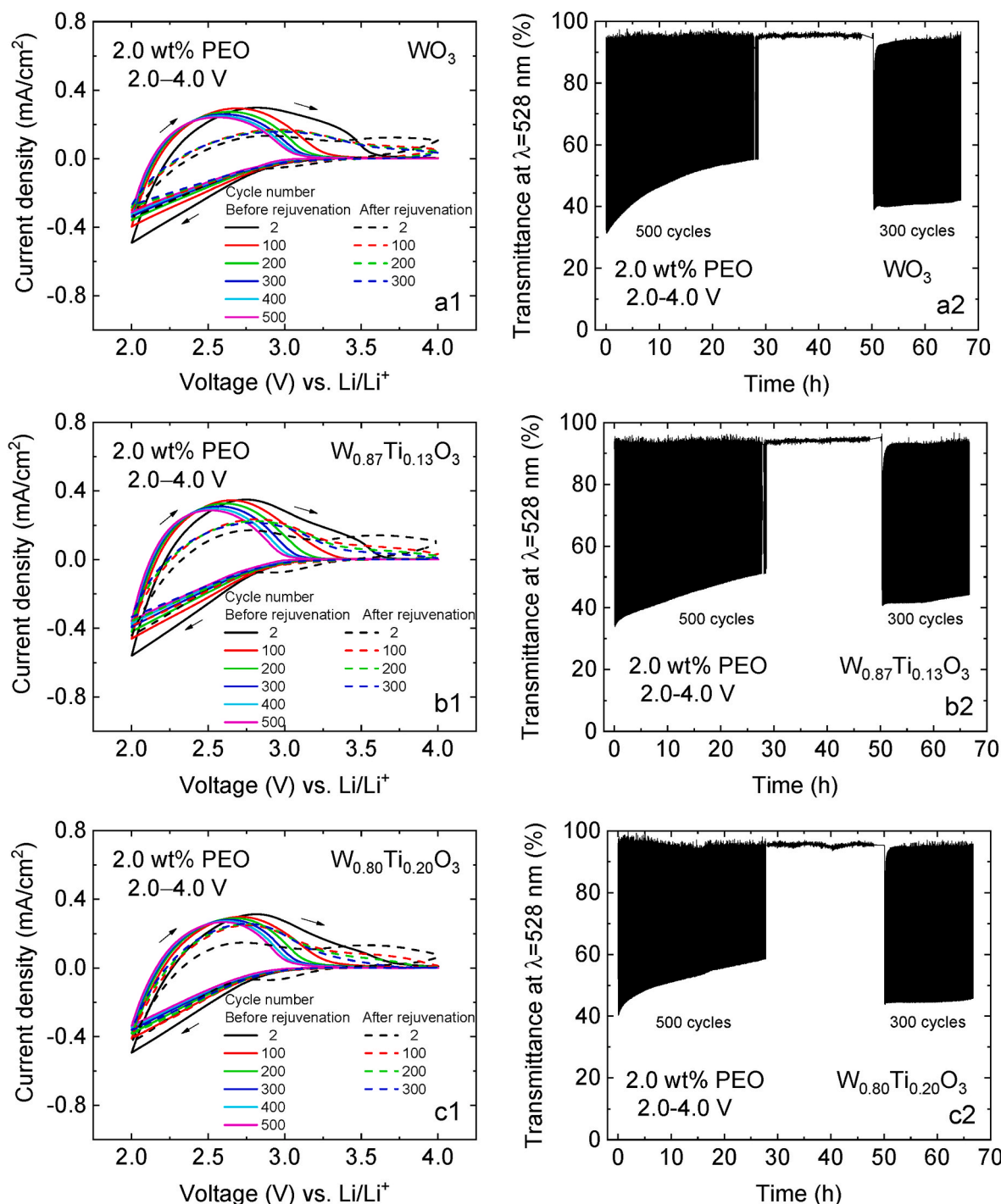


Fig. 2. Current density vs voltage for selected CV cycles in the 2.0–4.0-V potential range (left-hand panels) and corresponding optical transmittance measured at a wavelength of 528 nm (right-hand panels) for ~300-nm-thick films with the shown compositions. The electrolyte was 1 M LiClO₄-PC with 2.0 wt% of PEO. Voltammetry data are reported after the stated number of cycles for as-deposited films (solid curves) and after potentiostatic rejuvenation (dashed curves). Voltammetric scans were taken at 20 mV s⁻¹ in the directions indicated by arrows.

ref. 44 and the present work.

Fig. 6 reports the decline in charge capacity during cyclic voltammetry in the 1.5–4.0-V potential range and is drawn in analogy with Fig. 4. Obviously, $|Q|$ dropped sharply for as-deposited films, especially during the initial ~30 CV cycles. Rejuvenation treatment was able to restore 60–65% of the initial extracted and 90–95% of the initial inserted charge capacity. Renewed voltammetry led to a comparatively slow monotonic decline of $|Q|$ and after 500 CV cycles the extracted charge capacity reached 43, 21, and 32% of the initial values for WO₃,

W_{0.87}Ti_{0.13}O₃ and W_{0.80}Ti_{0.20}O₃ films, respectively, whereas the corresponding values for the inserted charge capacity were 24, 12, and 19%. The Li/(W + Ti) ratios in the dark state were significantly higher in the case of cycling in the 1.5–4.0-V range than for the 2.0–4.0-V range. We found x-values between 0.42 and 0.48 in the first cycles and significantly lower ones (0.37–0.39) immediately after rejuvenation. The values in the first cycles are quite close to the theoretical optimal value 0.5 [45], which indicates that the optical contrast observed in the first cycles in Fig. 5a2-c2 is close to optimum for these types of film.

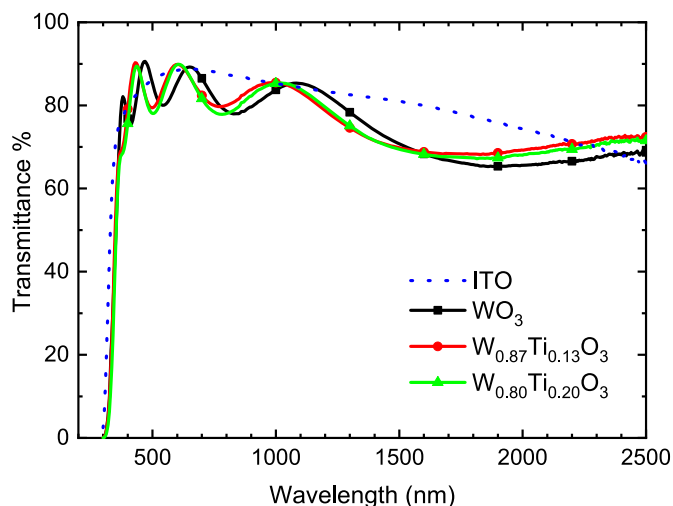
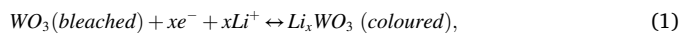


Fig. 3. Spectral transmittance for ~300-nm-thick films of as-deposited W oxide and W-Ti oxide. The dotted curve refers to data for the ITO-coated substrate.

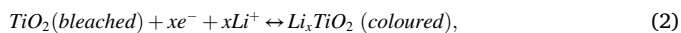
4. Discussion

We first discuss the properties of the as-deposited films. The stoichiometric compositions of tungsten oxide and titanium oxide are WO_3 and TiO_2 , respectively. These compounds are insulators with absorption edges above 3 eV and hence are transparent in the visible and most of the infrared wavelength ranges. The “stoichiometric” compositions of our Ti-doped tungsten oxide films would be $\text{W}_{0.87}\text{Ti}_{0.13}\text{O}_{2.87}$, and $\text{W}_{0.80}\text{Ti}_{0.20}\text{O}_{2.8}$, respectively. The experimentally measured compositions have significantly more oxygen, though. This points to a slight oxygen over-stoichiometry in our films, which probably is associated with the presence of OH groups, as discussed in previous work [24]. We infer that the probable oxidation states of the metal constituents are W^{6+} and Ti^{4+} , as expected for the stoichiometric compound. This assignment is also supported by the fact that the as-deposited films are highly transparent (Fig. 3) and hence they are sufficiently close to stoichiometry so that the optical properties are not affected.

Both WO_3 and TiO_2 are electrochromic and color under insertion of ions such as Li^+ . The coloration process for WO_3 and TiO_2 can be written as,



and



respectively.

The electrons are inserted into the films from the outer circuit in order to maintain charge neutrality. The optical absorption is due to electron transfer from W^{5+} to W^{6+} sites in the case of WO_3 and from Ti^{3+} to Ti^{4+} in the case of TiO_2 . The latter process is less likely in our films because the Ti content is low and most Ti atoms would not be close to another. However, we must also consider the possibility of charge transfer between W and Ti sites. In our films the initial dark state transmittance was lowest for WO_3 films and increased with Ti content. This indicates that $\text{W}^{5+} \leftrightarrow \text{W}^{6+}$ transitions are dominant and that $\text{W} \leftrightarrow \text{Ti}$ transitions are either insignificant or have low absorption strength.

We now continue the discussion by addressing durability issues. Additions of Ti to WO_3 are known to stabilize the amorphous state [20, 22]. The connection to electrochemical stability is not obvious, although it is clear that the amorphous state exhibits favorable EC properties, especially in the case of WO_3 . The effect of PEO additions to the electrolyte on durability is more difficult to understand. The composition of

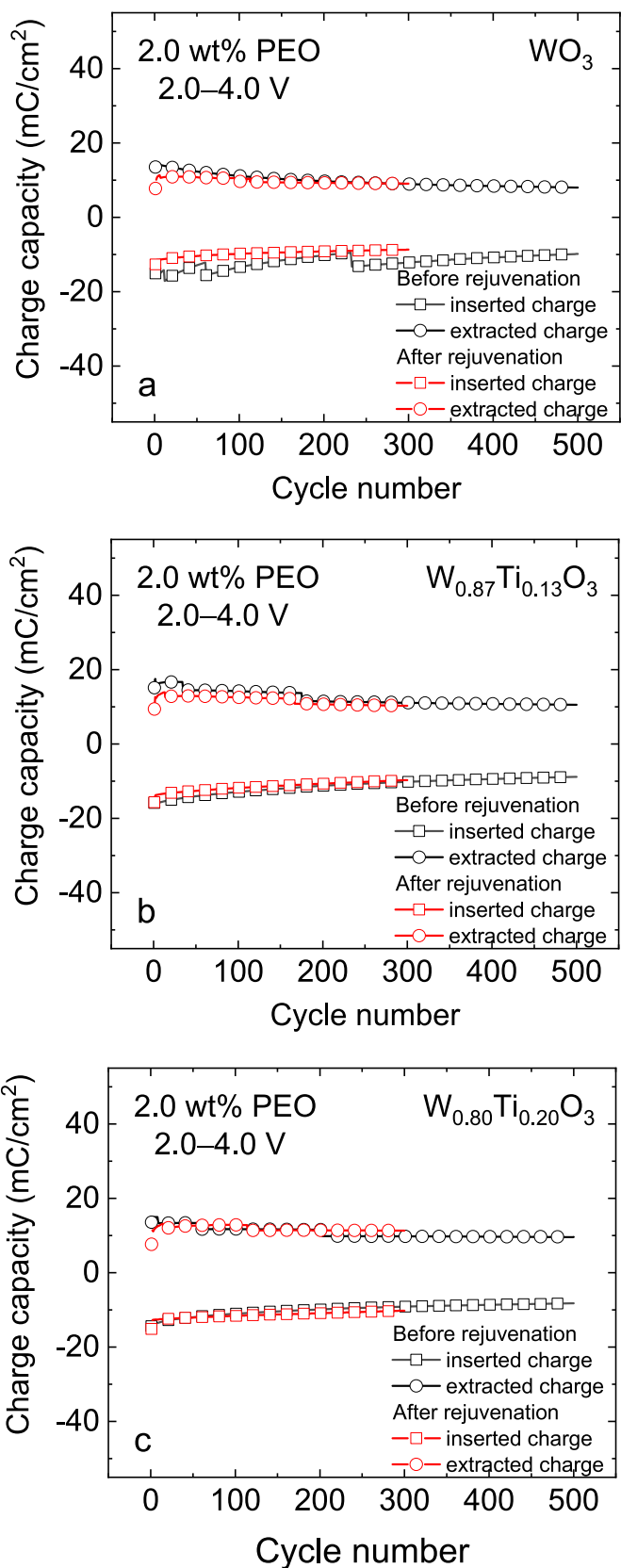


Fig. 4. Charge capacity vs number of CV cycles for ~300-nm-thick films with the shown compositions. Results are shown for inserted and extracted charge obtained from CV data (Fig. 2) in the 2.0–4.0-V potential range (vs Li/Li^+), before and after potentiostatic rejuvenation. The electrolyte was 1 M LiClO_4 -PC with 2.0 wt% of PEO.

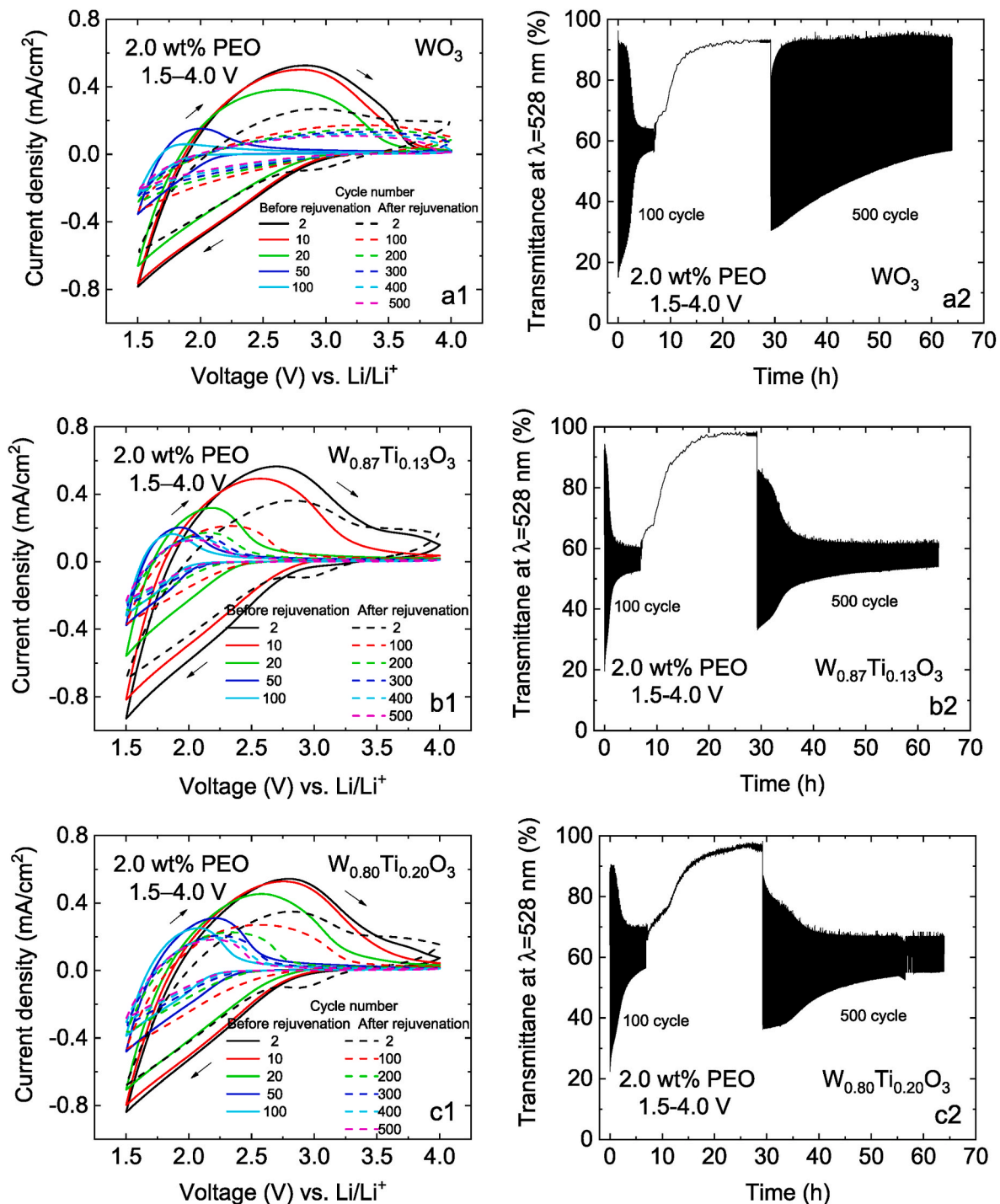


Fig. 5. Current density vs. voltage at selected CV cycles in the 1.5–4.0-V potential range (left-hand panels) and corresponding transmittance measured at a wavelength of 528 nm (right-hand panels) for ~300-nm-thick films with the shown compositions. The electrolyte was 1 M LiClO₄-PC with 2.0 wt% of PEO. Voltammetry data are reported after the stated number of cycles in the 1.5–4.0-V potential range (vs Li/Li⁺) for as-deposited films (solid curves) and after potentiostatic rejuvenation (dashed curves). Voltammetric scans were taken at 20 mV s⁻¹ in the directions indicated by arrows.

the electrolyte might affect the properties of the film-electrolyte interface and the possible presence of interlayer phases, often called interphases. Turning to the effects of the rejuvenation treatment, we can be more specific. From work in the battery field, it is known that a solid-electrolyte interphase forms upon polarization at high potentials [46]. It is probable that the same effect pertains to EC materials, and previous work found indications of carbonaceous deposits on WO₃ subjected to high potential treatment [41]. In the present study, we found, admittedly weak, evidence for the formation of a resistive layer

during rejuvenation, as discussed in connection with Fig. 2. The protective effect of such a solid-electrolyte interphase could explain the significantly improved durability of the films in the present study, subsequent to rejuvenation, that can be observed in Figs. 2 and 5. The protective effect becomes significant for PEO additions above about 1.0 wt% [44]. Previous studies using an electrolyte without PEO did not show improved durability after the rejuvenation treatment [24]. This may indicate that the addition of PEO leads to the formation of a more protective solid-electrolyte interphase layer.

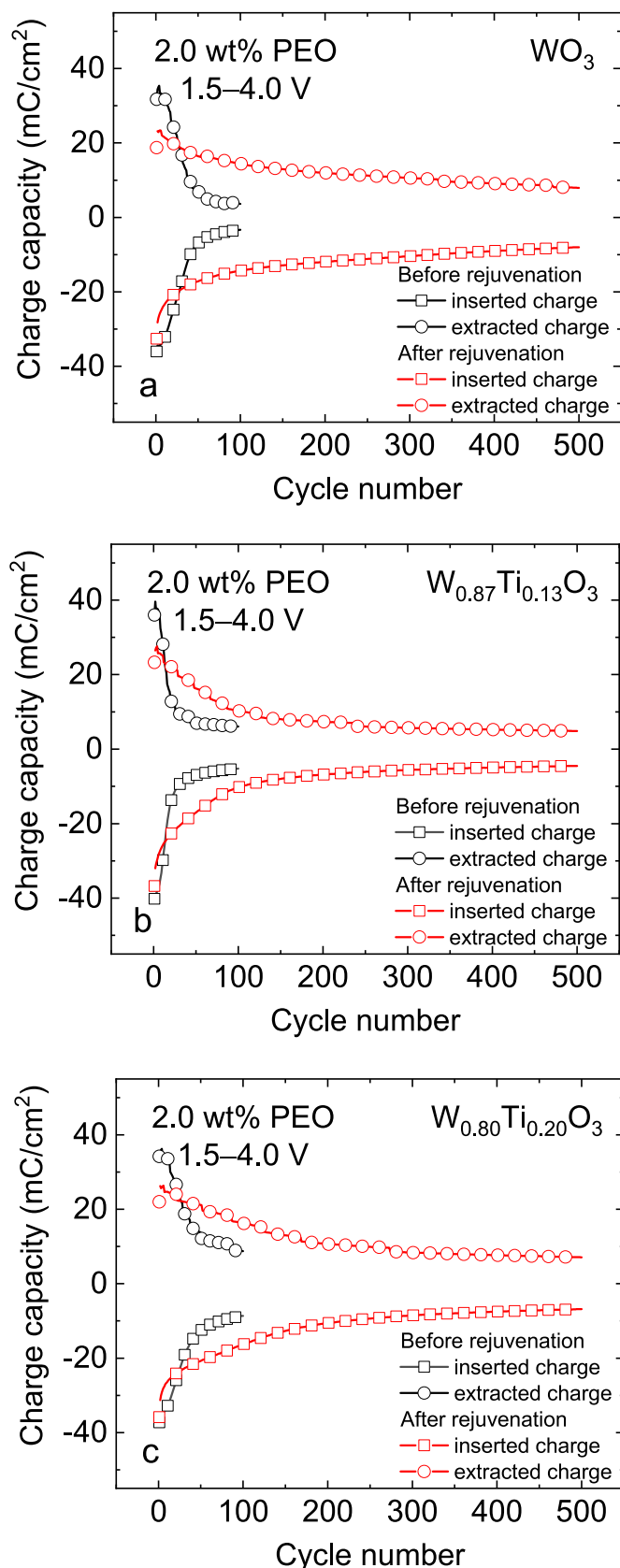


Fig. 6. Charge capacity vs number of CV cycles for ~300-nm-thick films with the shown compositions. Results are shown for inserted and extracted charge obtained from CV data (Fig. 5) taken in the 1.5–4.0-V potential range (vs Li/Li⁺), before and after potentiostatic rejuvenation. The electrolyte was 1 M LiClO₄-PC with 2.0 wt% of PEO.

Next we consider the possibility that the combination of Ti-doping and addition of PEO to the electrolyte leads to significant differences in EC properties. In order to assess the possible evidence for this we have compiled relevant data from our investigations and put them in tabular form. Tables 1 and 2 compare results on charge capacity and optical modulation range from the present investigation, using a LiClO₄-PC electrolyte with 2 wt% PEO, with results from our earlier work [24] which was performed on identically prepared films in an electrolyte without PEO; data are given for freshly deposited films, after finishing initial voltammetric cycling, subsequent to rejuvenation treatment, and, finally, after completing renewed cyclic voltammetry. It is clear from even a cursory examination of the results on Q and ΔT that the durability of EC W-oxide-based thin films is indeed a very complex issue. Nevertheless, several significant trends concerning Ti addition to the W oxide and PEO addition to the LiClO₄-PC electrolyte can be discerned. First we note that the previously established benefits of adding Ti to WO₃ [20–25] are confirmed for the electrolyte without PEO. It is seen that adding Ti to W oxide yields a slower decrease of Q and ΔT during voltammetric cycling both for as-deposited films and after potentiostatic rejuvenation. However, the increased stability comes at a cost, namely, as-deposited Ti-containing films exhibit a smaller transmittance modulation than as-deposited W oxide films. Secondly, the stability benefits of adding PEO to the electrolyte [44] are also observed; they most significant after the rejuvenation procedure.

We now discuss the interplay of Ti addition to the film and PEO addition to the electrolyte. Considering first the 2.0–4.0-V potential range, Table 1 leads to the following observations:

- The addition of PEO to the electrolyte gives a significantly diminished initial charge capacity and transmittance modulation both for as-deposited films and after potentiostatic rejuvenation. However, the magnitude of ΔT is still sufficient for most technical applications.
- We hypothesize that the diminished charge capacity in the PEO-containing electrolyte might be due to changes in the energy barrier for ion insertion at the film-electrolyte interface.
- Addition of Ti seems to have only minor effects on charge capacity and ΔT for WO₃ films in PEO-containing electrolytes.

Turning now to harsh voltammetric cycling in the 1.5–4.0-V potential range, Table 2 allows the following statements:

- The effect of PEO addition to the electrolyte on Q and ΔT appears to be varying and not entirely consistent.
- In almost all cases, there is very rapid degradation of the values of Q and ΔT . The degradation is significantly smaller after potentiostatic rejuvenation in the electrolyte with 2 wt% PEO.
- W oxide films cycled in an electrolyte with 2 wt% of PEO exhibit remarkable cycling durability after potentiostatic rejuvenation. Transmittance modulation is maintained despite a decrease in charge capacity, as was found in repeated experiments. These results point to structural and/or chemical changes in the film, perhaps similar to those observed after electrochemical treatment of W oxide films at high potentials [41].
- Addition of Ti to W oxide films in PEO-containing electrolyte has only small effects on the stability of as-deposited films, but actually decreases the stability of rejuvenated films.

To sum up, the benefits of adding Ti to W oxide films cycled in the PEO-containing electrolyte appear questionable and in some cases actually detrimental.

5. Conclusion

In the present study, we investigated the effect of Ti incorporation into W oxide thin films on electrochromic durability and potentiostatic rejuvenation in 1 M LiClO₄-PC electrolyte with 2 wt% PEO. Ti

Table 1

Density of inserted charge, Q , and transmittance modulation range at 528 nm, ΔT , for the shown PEO content and composition of ~300-nm-thick films. Data were taken on as-deposited and potentiostatically rejuvenated (as reported in the main text) films after the shown numbers of voltammetric cycles between 2.0 and 4.0 V with a scan rate of 20 mV s⁻¹. The electrolyte was 1 M LiClO₄-PC without and with 2 wt% PEO. Data without PEO were obtained from Ref. 24.

PEO content (%)	Film composition	As deposited				After rejuvenation			
		Q (mC/cm ²)		ΔT (%)		Q (mC/cm ²)		ΔT (%)	
		Cycle # 2	Cycle # 300	Cycle # 2	Cycle # 300	Cycle # 2	Cycle # 300	Cycle # 2	Cycle # 300
0	WO ₃	25.5	15.0	74	62	18.4	12.6	67	56
0	W _{0.87} Ti _{0.13} O ₃	20.4	13.5	66	57	15.3	11.8	60	54
0	W _{0.80} Ti _{0.20} O ₃	17.9	13.4	58	56	17.3	13.0	61	56
2	WO ₃	15.1	12.2	63	45	12.7	8.7	48	54
2	W _{0.87} Ti _{0.13} O ₃	15.8	10.2	61	49	15.7	9.7	45	50
2	W _{0.80} Ti _{0.20} O ₃	14.4	9.1	57	42	15.1	10.2	43	50

Table 2

Density of inserted charge, Q , and transmittance modulation range at 528 nm, ΔT , for the shown PEO content and composition of ~300-nm-thick films. Data were taken on as-deposited and potentiostatically rejuvenated (as reported in the main text) films after the shown numbers of voltammetric cycles between 1.5 and 4.0 V with a scan rate of 20 mV s⁻¹. The electrolyte was 1 M LiClO₄-PC without and with 2 wt% PEO. Data without PEO were obtained from Ref. 24.

PEO content (%)	Film composition	As deposited				After rejuvenation			
		Q (mC cm ⁻²)		ΔT (%)		Q (mC cm ⁻²)		ΔT (%)	
		Cycle # 2	Cycle # 100	Cycle # 2	Cycle # 100	Cycle # 2	Cycle # 100	Cycle # 2	Cycle # 100
0	WO ₃	51.7	8.8	86	21	30.9	6.3	64	16
0	W _{0.87} Ti _{0.13} O ₃	39.4	6.0	74	11	27.5	5.5	52	12
0	W _{0.80} Ti _{0.20} O ₃	40.9	8.2	72	14	33.2	5.5	41	10
2	WO ₃	36.0	3.3	78	7	32.6	14.3	52	55
2	W _{0.87} Ti _{0.13} O ₃	40.2	5.2	74	8	36.8	10.3	52	18
2	W _{0.80} Ti _{0.20} O ₃	37.3	8.6	68	13	35.8	16.3	51	29

incorporation resulted in small to moderate improvements in stability during voltammetric cycling in the commonly used 2.0–4.0-V potential range. However, no improvements were observed due to the addition of Ti in W oxide when cyclic voltammetry measurements were performed under harsh conditions in the 1.5–4.0-V range. In this large potential range, the transmittance modulation, as well as charge capacity after potentiostatic rejuvenation were actually better for films of WO₃ than for films of W_{0.87}Ti_{0.13}O₃ and W_{0.80}Ti_{0.20}O₃ when 2 wt% of PEO was present in the electrolyte. We note, in particular, that WO₃ films exhibited remarkable durability when cycled in the PEO-containing electrolyte after the rejuvenation procedure. This is possibly associated with the formation of a solid interphase layer due to the high-potential treatment.

To sum up, titanium addition to electrochromic tungsten oxide films is beneficial, at least in some cases, for voltammetric cycling in the 2.0–4.0-V range while pure tungsten oxide films are preferable for cycling in the wider potential interval 1.5–4.0 V. On a more general level, our work highlights that electrolyte modifications may be more important than increasing the stability of electrochromic thin films for the design of stable EC systems.

Credit author statement

İdris Sorar: Conceptualization, Methodology, Investigation, Formal analysis, Writing-Original Draft. **Gamze Atak:** Investigation. **İlknur Bayrak Pehlivan:** Conceptualization, Methodology, Investigation, Writing-Reviewing and Editing. **Claes G. Granqvist:** Writing-Reviewing and Editing, Supervision. **Gunnar A. Niklasson:** Resources, Writing-Reviewing and Editing, Supervision.

Declaration of competing interest

All authors declare that they have no conflicts of interest.

Data availability

Data will be made available on request.

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